AD/A-005 723

MAGNETIC AND ELECTRICAL PROPERTIES OF NOVEL COMPOUNDS IN THE ALKALINE EARTH - TRANSITION METAL - SULFUR AND SELENIUM SYSTEMS

Hugo Steinfink

Texas University at Austin

Prepared for:

Air Force Office of Scientific Research

October 1974

AFOSR - TR - 75 - 0303

Final Report

Magnetic and Electrical Properties of Novel Compounds in the Alkaline Earth - Transition Metal - Sulfur and Selenium Systems

by

Hugo Steinfink
Department of Chemical Engineering
The University of Texas at Austin
Austin, Texas 78712

October 1974

DDC
RECEIVED
FEB 26 1975
B

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER AFOSR - TR - 75 - 0303	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) MAGNETIC AND ELECTRICAL PROPERTIES OF NOVEL COMPOUNDS IN THE ALKALINE EARTH - TRANSITION METAL - SULFUR AND SELENIUM SYSTEMS		5. TYPE OF REPORT & PERIOD COVERED FINAL
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Hugo Steinfink		8. CONTRACT OR GRANT NUMBER(s) AFOSR-72-2199
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of Texas Department of Chemical Engineering Austin, Texas 78712		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS 9764-01 61102F 681306
11. CONTROLLING OFFICE NAME AND ADDRESS AF Office of Scientific Research (NE) 1400 Wilson Blvd. Arlington, VA 22209		12. REPORT DATE Oct 74
		13. NUMBER OF PAGES 18
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release: distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The interrelationship between crystal structure and electrical and magnetic compounds has been investigated. It has been shown that the physical behavior of Ba-Fe-S compounds can be predicted from a knowledge of the crystal structure and the presence of mobile or localized electrons. An unusually large range of temperature independent electrical conductivity has been observed for $BaCu_4S_3$.

DD FORM 1473   EDITION OF 1 NOV 65 IS OBSOLETE

PRICES SUBJECT TO CHANGE

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

Qualified requestors may obtain additional opies from the Defense Documentation Center; all others should apply to the Clearing House for Federal Scientific and Technical Information.

Reproduction, translation, publication, use and disposal in whole or in part by or for the United States Government is permitted.

Approved for public release; distribution unlimited.

Electrical and Magnetic Properties
Of Some Ba-Fe-S Compounds

This report covers the research effort from October 1, 1971 to August 31, 1974.

During the past several years we have synthesized a number of new barium-transition metal chalocogenide compounds. The crystal structures of most of these compounds are based on close packing of BaS_6 trigonal prisms with the transition metal filling some of the tetrahedral interstices. Table 1 summarizes the compounds whose structures have been determined and structural information can be found in references 1, 2, 3, 4, and 5. When iron is the transition metal some of the structures can be described in terms of FeS_4 tetrahedra which link by edge and/or corner sharing into infinite chains which are separated by about 6Å from adjacent chains. Other compounds have structures in which the FeS_4 tetrahedra are isolated, either singly or as bi- or trinuclear units. These arrangements produce one dimensional arrays of iron-iron and sulfer-iron interactions which are expected to give rise to interesting magnetic and electrical properties. It was the purpose of the research effort under this grant to evaluate the physical characteristics of these compounds and we concentrated on several iron compounds and on one copper phase.

Figure 1 shows the FeS_4 structural units for several iron compounds. Infinite linear chains of edge sharing tetrahedra are present in $Ba_9Fe_{16}S_{32}$; infinite double chains in $BaFe_2S_3$; zig-zag linear chains formed by corner sharing of trinuclear units in $Ba_7Fe_6S_{14}$; infinite linear chains of tetrahedra sharing corners in Ba_2FeS_3; infinite columns formed by four corner sharing FeS_4

in $Ba_6Fe_8S_{15}$. Isolated trinuclear units formed by a central tetra-hedron sharing one corner and one edge with two other tetrahedra are observed in $Ba_{15}Fe_7S_{25}$; isolated binuclear units in $Ba_9Fe_4S_{15}$; and isolated tetrahedra in Ba_3FeS_5.

Table 1.

Stoichiometries of compounds synthesized in Ba-T-X systems.
Where the anion is not indicated it is sulfur.

$$\underline{Ba\ :\ T\ :\ X}$$

Mn	Fe	Co	Ni	Cu	Zn	Cd
1 3	2 1 3	2 1 3			2 1 3	2 1 3
1 3Se	2 1 3Se					2 1 3Se
1 3Te						
	7 6 14					
	7 6 14Se					
	9 16 32					
	1 2 3					
	1 2 3Se					
	6 8 15					
	3 3 7Se					
	9 4 15					
	15 7 25					
2	3 1 5*	1 1 2	1 1 2			1 1 2
				1 4 3β (α)		
				1 2 2		
				1 2 2Se		

The formal transition metal valences that one expects from the stoichiometry of the compounds are summarized in Table 2. The magnetic moment for Fe^{+3} is about 5.9 B.M. and for Fe^{+2} and Fe^{+4} is about 5 B.M. so that

Table 2.

Formal transition metal charges based on stoichiometries.

Compound	No. Fe ions			Tetrahedral articulation
	divalent	trivalent	tetravalent	
Ba_2FeS_3	1			Corner, ∞ chain
$Ba_7Fe_6S_{14}$	4	2		Edge, corner and edge, ∞ chain
$BaFe_2S_3$	2			Edge, double ∞ chain
$Ba_6Fe_8S_{15}$	6	2		Corner and edge, ∞ column
$Ba_9Fe_{16}S_{32}$	2	14		Edge, ∞ chain
$Ba_{15}Fe_7S_{25}$	1	6		Isolated trinuclear unit
$Ba_9Fe_4S_{15}$		3		Isolated binuclear unit
Ba_3FeS_5			1	Isolated single tetrahedron

these values are expected for compounds in which the formal oxidation state of iron is tetra-, tri- or divalent and intermediate values are to be expected for mixed valence states. The measured magnetic moment, however, cannot distinguish between possible models for mixed valence states. The electrons on the iron atoms can be localized or fast exchange can occur so that an average value for Fe exists. However, in compounds whose structures consist of infinite chains the electrical resistivity is expected to be relatively high when localized electrons are present and should be relatively low when fast electron exchange, i.e. mobile electrons, are present. Furthermore, Mössbauer spectra should also indicate

the oxidation state for iron atoms, i.e. different isomer shifts
will be observed for different oxidation states. Table 3 summar-
izes the currently available data of the magnetic moments together
with the electrical parameters, band gaps, and isomer shifts
obtained from Mössbauer data.

The magnetic moment, the high electrical resistivity, and a
single large quadrupole splitting at room temperature with an
isomer shift value of 0.62 mm/sec. for Ba_2FeS_3 are consistent with
Fe^{+2} in agreement with the expected valence based on the stoichio-
metry of the compound. The magnetic moment for $Ba_7Fe_6S_{14}$ is con-
sistent with the averaged values for the iron oxidation states
expected on the basis of stoichiometry. The high electrical
resistivity would indicate that the electrons are localized on
the crystallographic iron sites or that delocalization occurs
only within the trinuclear unit but no electron transport occurs
between the units. A close examination of the environment of the
three iron atoms in the basic trinuclear unit in this compound
indicates that the iron atoms have a slightly different atomic
environment and that three sets of quadrupole split lines might
be expected at room temperature. Figure 2 shows the Mössbauer
spectrum of $ba_7Fe_6S_{14}$ and indeed three sets of quadrupole split
lines are evident. The interpretation of these data leads to the
conclusion that the electrons are delocalized and that the delo-
calization is restricted to the trinuclear unit. The 3.67Å distance
between Fe-Fe located in the tetrahedral interstices or the corner
sharing tetrahedra prevents the overlap of orbitals between the
units and no continuous conduction band is formed.

In $Ba_6Fe_8S_{15}$, whose fundamental structural unit is an infinite
columnar arrangement of FeS_4 tetrahedra, the magnetic moment is
consistent with the average expected for 2 Fe^{+3} and 6 Fe^{+2} on the

Table 3.

Summary of paramagnetic moment, room temperature
electrical resistivity, band gap and isomer shifts.

mpound	Effective moment, B.M.	Room temperature electrical resistivity, ohm-cm	E_g, e.v.	Room temperature isomer shift,* mm/sec.
$_2FeS_3$	5.29	10^4	0.60	0.62
$_7Fe_6S_{14}$	5.70	10^3	0.62	0.49, 0.36, 0.36
Fe_2S_3	4.85	0.5	0.16	0.41
$_6Fe_8S_{15}$	5.57	1.0	0.31	0.47
$_9Fe_{16}S_{32}$		1.0	0.14	0.20
$_{15}Fe_7S_{25}$	5.5	10^5		0.20, 0.60
$_3FeS_5$	5.1	10^5		0.20

* Relative to Fe foil

basis of the stoichiometry. The electrical resistivity is quite
low indicative of rapid electron exchange. Thus all the iron
atoms should appear the same and indeed the Mossbauer spectrum
shows a single quadrupole splitting at room temperature with an
isomer shift that can be interpreted as due to an iron atom of an
intermediate oxidation state.

BaFe$_2$S$_3$ has a magnetic moment as expected for Fe^{+2} but
the electrical conductivity is low and thus indicative of mobile
electrons. On the basis of stoichiometry one would expect that
only divalent iron should be present and the low resistivity is
rather unexpected. The Mössbauer spectrum shows a single quadru-
pole splitting indicating that all iron atoms are in the same
environment; the isomer shift is almost exactly intermediate

between the extremes of 0.20 and 0.60 which we have observed for Fe^{+3} and Fe^{+2} respectively. All the evidence points to the delocalization of nearly one half electron per iron atom.

The structure of $Ba_9Fe_{16}S_{32}$ consists of an infinite chain of edge-sharing FeS_4 tetrahedra and the Mössbauer data show a single quadrupole at room temperature with an isomer shift of 0.20 mm/sec. consistent with Fe^{+3}. For this stoichiometry the formal charge distribution must be 14 Fe^{+3} and 2 Fe^{+2}. The Mossbauer results indicate the equivalence of all Fe and therefore the electrons should be mobile. The resistivity of this material is of the same order of magnitude as for $Ba_6Fe_8S_{15}$ and $BaFe_2S_3$ and mobile electrons are presnet.

The measured magnetic moment of $5.5u_B$ for $Ba_{15}Fe_7S_{25}$ is in good agreement with the average spin only magnetic moment expected for six trivalent and one divalent iron atoms. The Mössbauer spectra show quadrupole split lines with isomer shifts of 0.20 mm/sec. at 300^OK and 0.31 mm/sec. at 78^OK, consistent with the values found for Fe^{+3}. A close examination of the Mössbauer spectrum indicated the presence of a small shoulder which we interpret to be due to one Fe^{+2} in the structure. A theoretical curve was calculated on the basis of a mixture of 6 Fe^{+3} and 1 Fe^{+2} using isomer shifts of 0.2 and 0.6 mm/sec. and, indeed the theoretical curve reproduced the observed features. It is concluded, therefore that the oxidation state of iron in this compound consists of a 6:1 ratio of trivalent to divalent iron and that the electrons are localized on the crystallographic sites. On the basis of the Mössbauer results this material can be expected to exhibit a high value of the electrical resistivity, comparable to that observed for $Ba_9Fe_{16}S_{14}$. The electrical measurements confirmed that this

material is a high resistivity semi-conductor, Table 3.

The measured effective magnetic moment of 5.1 μ_B for Ba_3FeS_5 corresponds closely to the value expected for Fe^{+2} or Fe^{+4}. The isomer shifts obtained from Mössbauer spectra at $300^O K$ and $78^O K$ are 0.17 and 0.26 mm/sec. respectively. At both temperatures only one quadrupole splitting is observed of 0.50 mm/sec. The value of the isomer shift is consistent with Fe^{+3} on the basis of our results in other related compounds in the Ba-Fe-S system. The apparent disagreement between the observed magnetic moment, consistent with either Fe^{+2} or Fe^{+4} and the Mössbauer isomer shift, consistent with Fe^{+3}, can be resolved by the supposition that back donation of electrons occurs. It becomes difficult to define a precise value of the oxidation state of iron within the tetrahedron if this back donated electron density is delocalized over the orbitals constrained to the tetrahedron. The delocalized electrons would not contribute significantly to the measured paramagnetic moment, but would cause the isomer shift to resemble that for Fe^{+3}. The electrical resistivity of this material is expected to be fairly high because the FeS_4 units are isolated, and the measurement yields as value of about 10^5 ohm-cm, Table 3. The results of this research can be found in references 6 and 7.

As a result of the magnetic and electrical measurements combined with the structural information the interrelationship between physical properties and atomic structure for these compounds has become clear. We expect to continue work in this system and use this knowledge to guide us toward experiments that, hopefully, may lead to materials with technologically useful properties.

Electrical Properties of $BaCu_4S_3$

$BaCu_4S_3$ has an $\alpha-\beta$ phase transition at $640 \pm 10^{\circ}C$ and melts at $879 \pm 10^{\circ}C$. We synthesized this material and investigated the crystal structures and electrical behavior. The α and β phases have very similar orthorhombic structures and consist of BaS_6 trigonal prisms which share the triangular faces to form an infinite chain. Adjacent chains are displaced so that sulfur atoms cap one of the rectangular faces in the α phase and two faces in the β phase. The unique aspect in these structures is the inter-weaving of infinite copper chains, zig-zag in the α and linear in the β phase, (8). This unusual array of copper atoms induced us to expend a considerable effort on single crystal growth and the evaluation of the electrical behavior.

Electrical resistivity measurements were performed on pressed bars and on polycrystalline chunks. The pressed bars had dimensions of about 2.5 cm x 0.5 cm x 0.1 cm, and were obtained by pressing fine powder into a die, under a pressure of 12,000 psi, followed by heating in a vacuum at a temperature of $400^{\circ}C$ for 48 hours. The polycrystalline chunks were selected from the reaction product. Their dimensions were about 0.2 cm x 0.2 cm x 0.1 cm. The four-probe method of measurement was used, except for the very small samples which were measured by the two probe method.

One of the important problems in carrying out the measurements was the electrical contacts between the copper leads and the sample. When chunks were used, the contacts were made with silver paint. Better contacts can, in principle, be made when using pressed-bars. The current-carrying copper leads may be mounted into the die when the powder is poured in and pressed together.

Good contacts were obtained in this way, although the sample frequently broke when removed from the die. The low temperature measurements, to $78^{O}K$, were performed in a specially designed apparatus while the high temperature measurements were performed in vacuum or in a flowing nitrogen gas stream. The temperature was measured by a chromel-alumel thermocouple mounted next to the sample.

Typical results are shown in Figures 3 and 4. The resistivity of the α-BaCu$_4$S$_3$ pressed bar is almost independent of temperature. The resistivity of the β-BaCu$_4$S$_3$ chunk has a behavior characteristic of a degenerate semi-conductor. The range of temperature independence for the α form is very unusual and this observation has been repeated on several different samples. We intend to do considerably more work on this material and we shall attempt to grow single crystals large enough for various measurements in order to elucidate the mechanism responsible for this behavior.
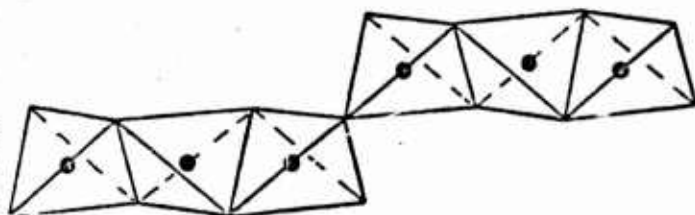
Ba : Fo : S
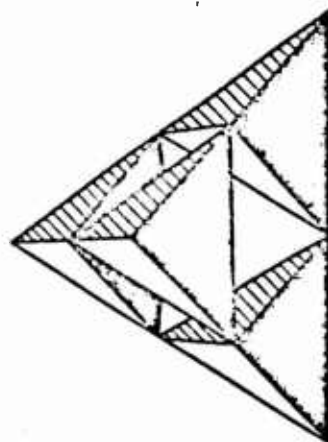
(a) 9:16:32

(b) 1:2:3

(c) 7:6:14

(d) 2:1:3

(e) 6:8:15

(f) 15:7:25

-16-
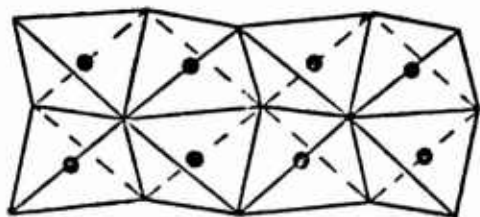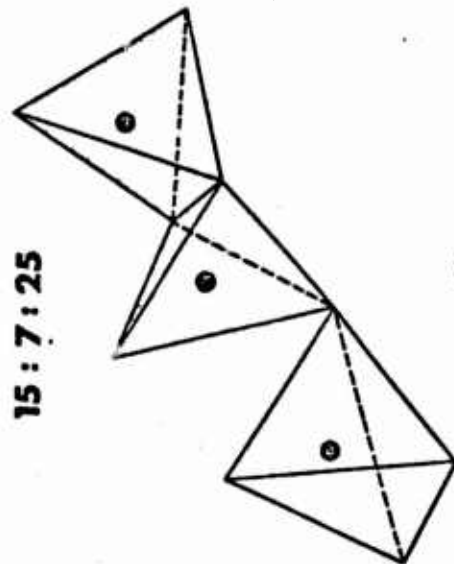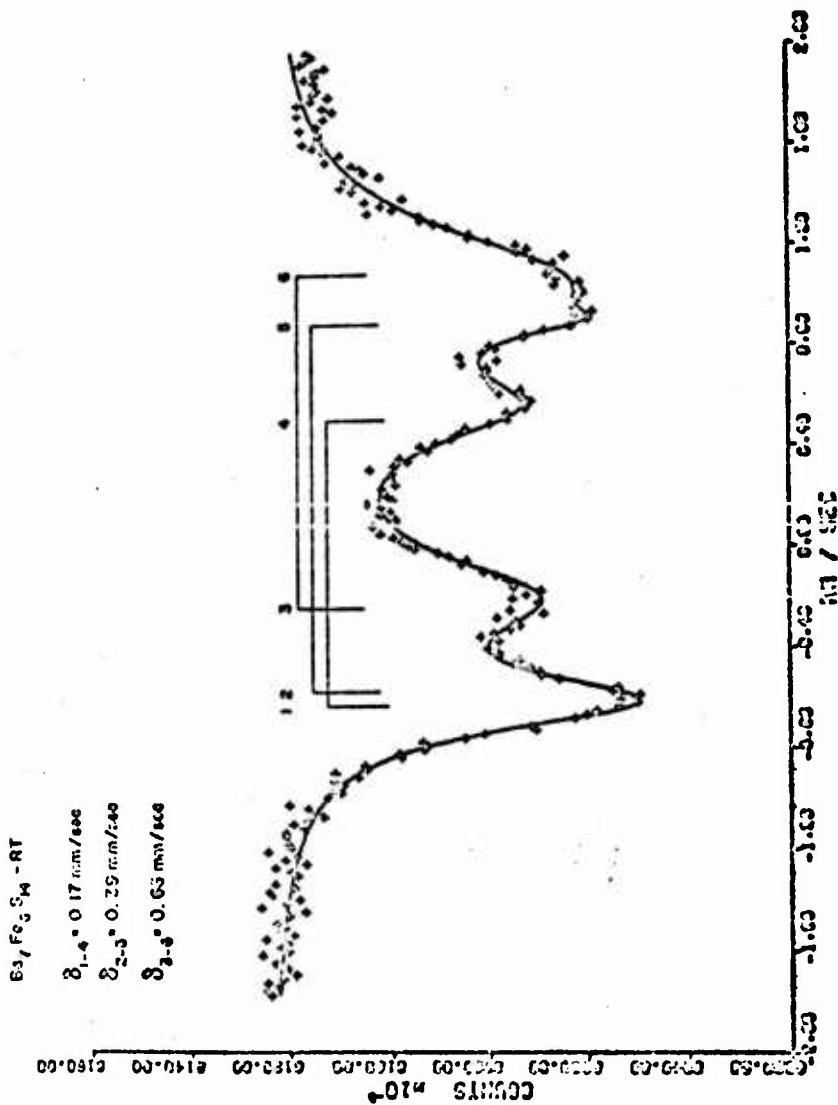
Fig. 2   Room temperature Mössbauer spectrum of $Ba_7Fe_6S_{14}$. Brackets denote the matching of quadrupole split lines.

-//-

- 12 -
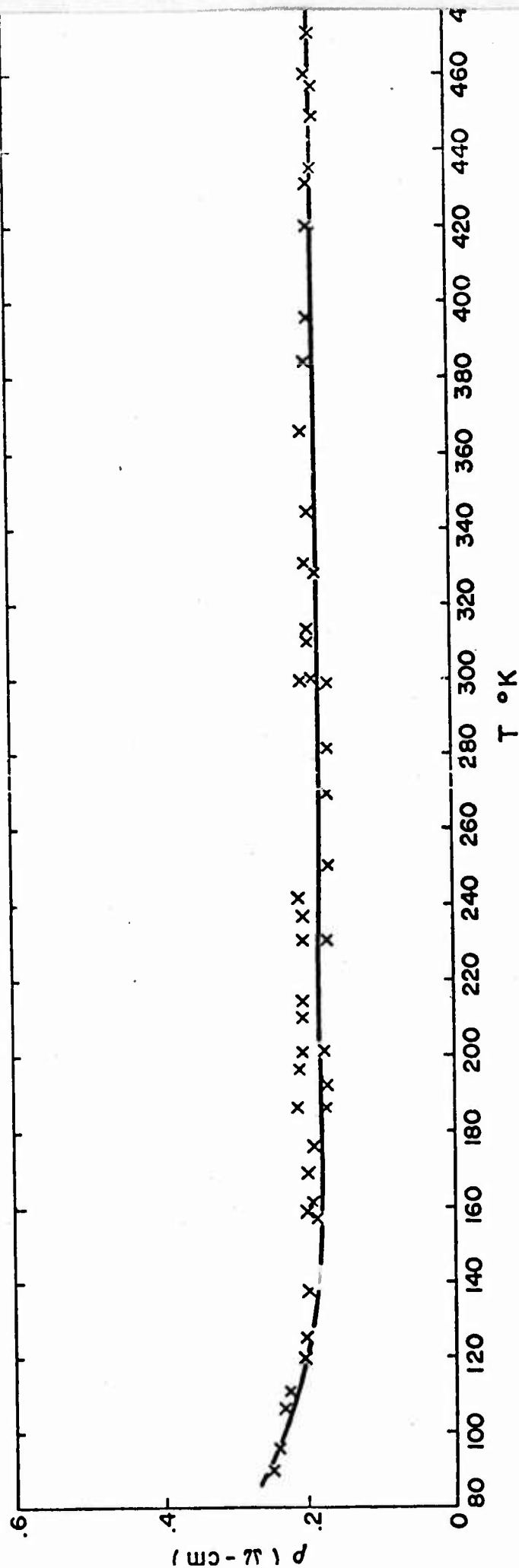
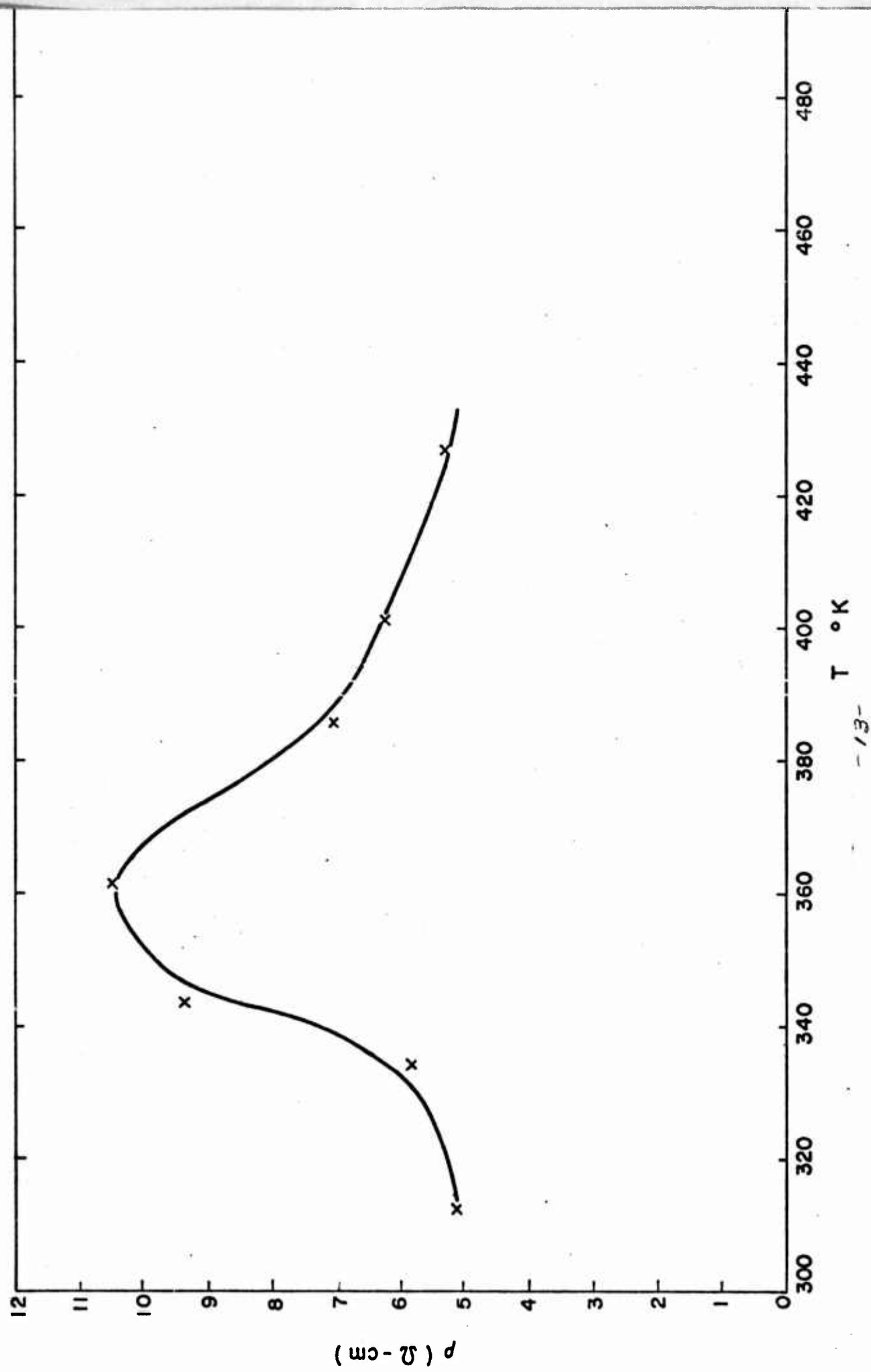Fig. 4   Electrical resistivity vs T for a PbSe...

-13-

REFERENCES

1. I. E. Grey, H. Hong and H. Steinfink, Inorganic Chemistry, 10, 340 (1971).

2. I. E. Grey and H. Steinfink, Inorganic Chemistry, 10, 691 (1971).

3. H. Y. Hong and H. Steinfink, J. Solid State Chemistry, 5, 93 (1972).

4. H. Steinfink, H. Hong and I. Grey, National Bureau of Standards Special Publication 364, Proceedings of 5th Materials Research Symposium, 1972.

5. I. E. Grey, J. Solid State Chemistry 11, 128 (1974).

6. W. M. Reiff, I. E. Grey, A. Fan, Z. Eliezer and H. Steinfink, J. Solid State Chemistry, In Press.

7. J. T. Lemley, J. M. Jenks, J. T. Hoggins, Z. Eliezer and H. Steinfink, J. Solid State Chemistry, Submitted for Publication.

8. J. E. Iglesias, K. E. Pachali and H. Steinfink, Materials Research Bulletin, 7, 1247 (1972).

Research Participants

The following personnel participated as predoctoral research assistants:

J. E. Iglesias

A. Chan

The following personnel held post doctoral research appointments:

K. Pachali

J. T. Lemley

J. E. Iglesias

Z. Eliezer

Publications

J. E. Iglesias, K. E. Pachali and H. Steinfink "The Crystal Structures and Phase Transition of α and β $BaCu_4S_3$." Materials Research Bulletin 7, 1247 (1972).

W. M. Reiff, I. E. Grey, A. Fan, Z. Elieaer and H. Steinfink "The Oxidation State of Iron in Some Ba-Fe-S Phases: A Mossbauer and Electrical Resistivity Investigation of Ba_2FeS_3, $Ba_7Fe_6S_{14}$, $Ba_6Fe_8S_{15}$, $BaFe_2S_3$, and $Ba_9Fe_{16}S_{32}$. Journal of Solid State Chemistry, In Press.

J. T. Lemley, J. M. Jenks, J. T. Hoggins, Z. Eliezer, and H. Steinfink, "$Ba_{15}Fe_7S_{25}$ and Ba_3FeS_5: Crystal Structures, Mossbauer, Magnetic and Electrical Behavior." Journal of Solid State Chemistry, Submitted for Publication.

In addition to the above it is anticipated that at least two additional publications covering work done on the Ba-Fe-S system and on $BaCu_4S_3$ will result from work done under this grant.

Patents

No application for patents have been filed at this time as a result of this work.

Dissertation, Ph.D.

"The Crystal Chemistry of Some Ternary Sulfides and Selenides, and the Crystal Structure of Gd_5Si_4." J. E. Iglesias, December 1971.